



UNIVERSITI PUTRA MALAYSIA

***CHEMICAL AND MINERALOGICAL FORMS OF
HEAVY METALS IN SEDIMENTS AT LANGAT
RIVER, SELANGOR***

NUR ALIAA SHAFIE

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By

NUR ALIAA SHAFIE

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfillment of the Requirement for the Degree of Master Science**

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree Master of Science

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By

NUR ALIAA SHAFIE

March 2013

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Faculty: Environmental Studies

Langat River is one of the most important rivers in Selangor that caters drinking water sources for up to 1.2 million populations within the basin. In 2004, Langat River has been recognized as one of the Hydrology for the Environment, Life and Policy (HELP) river basin. An explanatory study was carried out at 22 sampling stations along the river. The sediment samples (0 – 20cm) were collected for metal speciation (Cd, Cu, Zn, As, Pb) using sequential extraction technique (SET) and analyzed via the inductively coupled plasma-mass spectrometry (ICP-MS). Parameters such as pH, Eh, electrical conductivity (EC), salinity, loss on ignition (LOI), cation exchange capacity (CEC) and particle size analysis (PSA) were also determined. The sediment mineralogy was determined using X - Ray diffraction (XRD). This study revealed that sediment was predominantly by Pb(150.29µg/g)>Cu(57.91µg/g)>As (37.40µg/g)>Zn (30.46µg/g)>Cd (0.061µg/g). There is a significant correlation among pH, Eh, EC, Ca²⁺, Cu, Zn, As with Pb at r=-0.234 - 0.354 (p<0.01). The associations among metals (Cd, Cu, Zn and As)

with sediment characteristics variables were due to the factor that each variables poses towards the bioavailability of metals in the environment. The sediment mineralogy also played a significant role in controlling the fate of metal. The mineralogy that is dominant by quartz correlated with Zn, As and Pb at $p < 0.1$ confirmed that mineralogy controlled the metals accumulation. The fractionation indicate the metals mobility were $\text{Cu} > \text{Cd} > \text{Zn} > \text{As} > \text{Pb}$ in decreasing order. The association of Cu (94.61%) and Cd (64.80%) were described to be strongly attached with the non residual phase. This is contradicting with Zn (52.46%), As (66.43%) and Pb (92.21%) that accounted as the least mobile metals as a result of strong association with the residual phases. This suggests that Cu and Cd are more prone to the remobilization in the overlying water compared to Zn, As and Pb. The principal component analysis (PCA) exhibited salinity as the controlling factor in the river clusters separation. This is proven by the correlation of salinity with CEC, LOI, Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cd, Cu and Zn at PC1. This suggests that natural sources are the highest percentage of contribution (31.92%). The dendrogram displayed stations LA 2, LA 3, LA 4, LA 5 and LA 8 as highly contaminated by Cu, Zn and As. This is supported by sediment quality guidelines (SQGs) that exhibited As as the most contaminated with 100% exceeding the permissible limits. Therefore, it is crucial to understand the interactions of specific metals in the sediment in order to controls the release, remobilization and absorption. These findings are expected to update the current status of the heavy metal pollution status as well as creating awareness concerning the security of the river water as a drinking water sources.

Keyword: sediment, heavy metal, sequential extraction technique, mobility.

Abstrak ini yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SIFAT-SIFAT KIMIA DAN MINERALOGI LOGAM BERAT DALAM SEDIMEN DI SUNGAI LANGAT, SELANGOR

Oleh

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Sungai Langat merupakan sungai yang paling penting di Selangor yang bertindak sebagai sumber air minuman untuk lebih 1.2 juta penduduk di lembangan Sungai Langat. Pada tahun 2004, Sungai Langat telah diiktiraf sebagai salah satu lembangan sungai dibawah naungan Hidrologi bagi Alam Sekitar, Kehidupan dan Dasar (HELP). Satu kajian telah dijalankan di 22 stesen persampelan di sepanjang Sungai Langat. Sampel sedimen (0 - 20cm) telah diambil untuk penspesian logam (Cd, Cu, Zn, As, Pb) melalui teknik pengekstrakan berjujukan (SET) dan dianalisis menggunakan induksi plasma spektrometri jisim (ICP-MS). Parameter seperti pH, Eh, kekonduksian elektrik (EC), kemasinan, kehilangan menerusi pembakaran (LOI), kapasiti penukargantian kation (CEC) dan analisis saiz zarah (PSA) juga telah ditentukan. Mineralogi sedimen juga telah ditentukan dengan menggunakan X-Ray pembelauan (XRD). Kajian ini menunjukkan bahawa sedimen didominasi oleh Pb(150.29 μ g/g)>Cu(57.91 μ g/g)>As(37.40 μ g/g)>Zn(30.46 μ g/g)>Cd(0.061 μ g/g). Pb menunjukkan hubungan yang

signifikan dengan pH, Eh, EC, Ca^{2+} , Cu, Zn pada $r = -0.234 - 0.354$ ($p < 0.01$). Penyatuan yang signifikan diantara logam berat (Cd, Cu, Zn dan As) dan pembolehubah ciri-ciri sedimen adalah disebabkan oleh faktor yang dimiliki oleh setiap pembolehubah terhadap bioavailabiliti logam berat didalam alam sekitar. Mineralogi sedimen memainkan peranan penting dalam mengawal nasib logam. Mineralogi sedimen di Sungai Langat didominasi oleh kuarza menunjukkan kolerasi yang signifikan dengan Zn, As dan Pb pada $p < 0.1$. Ini mengesahkan bahawa mineralogi mempunyai kawalan terhadap pengumpulan logam berat didalam sedimen. Penspesian menunjukkan pergerakan logam didominasi oleh $\text{Cu} > \text{Cd} > \text{Zn} > \text{As} > \text{Pb}$. Cu (94.61%) dan Cd (64.80%) dikenalpasti mempunyai daya tarikan yang tinggi dengan fasa bukan sisa. Ini bercanggah dengan Zn (52.46%), As (66.43%) dan Pb (92.21%) yang didapati sebagai logam berat yang paling kurang bergerak hasil daripada penyatuan yang kukuh dengan fasa sisa. Ini menunjukkan bahawa Cu dan Cd adalah lebih cenderung kepada remobilisasi di dalam permukaan air berbanding Zn, As dan Pb. Analisis komponen utama (PCA) mempamerkan kemasinan sebagai faktor kawalan yang penting didalam pemisahan kelompok sungai. Ini dibuktikan oleh korelasi kemasinan dengan CEC, LOI, Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cd, Cu dan Zn di PC1. Ini membuktikan bahawa sumber-sumber semula jadi adalah penyumbang kepada peratusan tertinggi di Sungai Langat (31.92%). Dendogram memaparkan stesen LA 2, LA 3, LA 4, LA 5 dan LA 8 sebagai paling tercemar oleh Cu, Zn dan As. Ini disokong oleh garis panduan kualiti sedimen (SQGs) yang menunjukkan As sebagai logam paling tercemar dengan 100% melebihi had yang dibenarkan oleh SQGs. Pengetahuan yang sangat mendalam dalam pemahaman interaksi logam tertentu adalah sangat penting untuk mengawal pelepasan, remobilisasi dan penyerapan logam berat didalam sedimen. Penemuan ini dijangka dapat mengemaskini status semasa

pencemaran logam berat serta mewujudkan kesedaran mengenai keselamatan air sungai sebagai sumber air minuman.

Kata kunci: sedimen, logam berat, teknik pengekstrakan berjujukan, mobiliti.



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I certify that a Thesis Examination Committee has met on 7 March 2013 to conduct the final examination of Nur Aliaa binti Shafie on her thesis entitled "Chemical and Mineralogical Forms of Heavy Metals in Sediments of Langat River, Selangor, Malaysia." in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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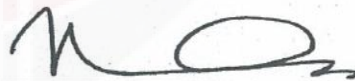
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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and it's not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

NUR ALIAA SHAFIE

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